SCIENCE FOR CERAMIC PRODUCTION

ACTIVITY OF A BLOCK CELLULAR CATALYST WITH A MODIFIED SUBSTRATE

A. I. Kozlov,[1] E. S. Lukin,[1] I. A. Kozlov,[1] V. P. Kolesnikov,[1] and V. N. Grunskii[1]

The effect of active substrate on the process of liquid-phase reduction of *para*-nitrotoluene (P-NT) on a highly porous cellular palladium catalyst (HPCPC) is studied. The rate of the reducing reaction for 50% transformation of the initial nitric compound in the temperature range of 52 – 58°C is determined for the HPCPC using various oxides and their sulfatized forms as active substrate. It is shown that the highest velocity of P-NT hydration is reached using the HPCPC with an active substrate made of sulfatized ZrO_2 and γ-Al_2O_3. The constants of reducing P-NT and the load of the nitric compound on the catalyst are calculated; the highest values are found in the HPCPC with a sulfatized ZrO_2 substrate.

One of topical problems in the production of heterogeneous deposited catalysts is the search for new materials to be used as carriers. The need to use a carrier is determined by several reasons:

– thermal stabilization and preventing sintering of catalyst in service [1];

– resistance of catalyst to poisoning;

– decreasing cost production by diluting expensive components;

– increasing strength and decreasing hydraulic resistance;

– possibility of easy separation of catalyst from the reaction mixture for the purpose of its multiple reuse without decreasing its activity.

Researchers propose different variants for solving these problems. Thus, the authors in [2] introduce modifying additives, such as cerium, zirconium, etc. to improve the thermal stability of catalyst and also its resistance to poisons.

The researchers at the D. I. Mendeleev Russian Chemical Engineering University propose a catalyst carrier represented by a highly porous cellular material (HPCM) produced by the method of duplicating an open-cellular foam-polyurethane matrix with a ceramic material based on aluminum oxide (RF patent No. 2233700). According to the main principles of D. V. Sokolovskii's theory of catalysts [3], catalyst carriers should have an extended surface, certain pore sizes, and other physical parameters.

Products made of the HPCM fired at 1350 – 1450°C contain mainly α-Al_2O_3 with a specific surface area of about $1\ m^2/g$, which restricts the production of catalysts with a variable content and dispersion of active components and with a homogeneous distribution over the carrier surface. Therefore the deposition of a secondary oxide coating on products with a cellular structure produces carriers with an extended specific surface area and a highly porous structure (Fig. 1).

It is known that the surface area of a catalyst primarily depends on the method of its preparation. The most efficient method for obtaining a highly extended surface is precipitating the catalytically active component in the form of a hydroxide or a carbonate, which produces a gel-like precipitate; after its drying and calcination, water and CO_2 are removed and, as a consequence, we obtain high porosity and, accordingly, a larger surface in the deposited layer [4].

This technique was found successful in producing catalysts by extrusion or tableting, since mixtures are prepared using aluminum oxide in the form of γ-Al_2O_3 with a well extended surface: up to $220\ m^2/g$ (RF patent No. 2233700). When the HPCM based on α-Al_2O_3 is used as a carrier, γ-Al_2O_3 or another oxide should be deposited on the corundum substrate to increase the surface area of porous bridges.

Several methods are known for depositing active material on α-Al_2O_3. In the present study we use the method of impregnating HPCM with solutions of metal nitrates, hydrochloric Al_2O_3 sol, or SiO_2 sol. It is known that catalytic activity depends not only on the surface area, but on acidity as

[1] D. I. Mendeleev Russian Chemical Engineering University, Moscow, Russia; Nevinnomyssk Technological Institute (branch) of SevKavGTU University, Nevinnomyssk, Russia.
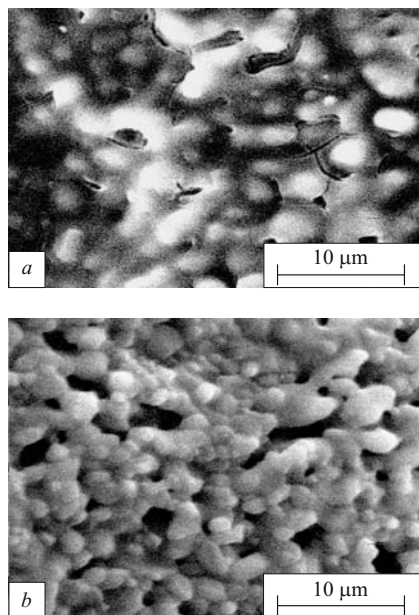
Fig. 1. Structure of bridges between cells without sol (*a*) and with sol (*b*): *a*) relative surface area of pores 2.6%, their size 0.8 – 1.2 μm; *b*) relative surface area of pores 33.8%, their size 1.5 – 2.2 μm.

Fig. 2. Time variation in the amount of absorbed hydrogen in hydrating P-NT on HPCPC with different active substrates (*a*) and linearized dependences for the velocity constant of the first-order reaction for hydrogen (*b*): *a*: □) 2.70% Pd/SiO$_2$, ▲) 2.35% Pd/TiO$_2$ (sulfatized), ○) 3.00% Pd/ZnO, ●) 2.44% Pd/Al$_2$O$_3$, ✳) 1.89% Pd/ZrO$_2$ (sulfatized); *b*: □) 2.70% Pd/SiO$_2$, ◆) 2.76% Pd/TiO$_2$, ×) 2.76% Pd/ZrO$_2$, ○) 3.00% Pd/ZnO, ●) 2.44% Pd/Al$_2$O$_3$, ▲) 2.35% Pd/TiO$_2$ (sulfatized), ✳) 1.89% Pd/ZrO$_2$ (sulfatized).

well. Therefore, we have investigated various types of active substrates with different surface geometry and different pH.

Acidity on a catalyst surface can be modified currently within wide limits by using different types of carriers, from pure aluminosilicate to sulfatized TiO$_2$ and zirconium. Sulfatized TiO$_2$ was applied as follows. A HPCM sample was impregnated with tetrabutoxytitanium solution diluted with isopropanol in the ratio of 1 : 1 (twice or more times) until getting a sample containing 6% TiO$_2$. After each impregnation the sample was heat-treated at 500°C. Next, the samples with deposited TiO$_2$ were immersed in 1-N solution of sulfuric acid and then fired at 550°C. Sulfatized ZrO$_2$ was deposited using the same method, except for the initial soluble zirconium salt. For reference purposes we also give experimental data using ZnO with an obviously alkaline surface as catalyst carrier.

Later palladium nitrate from a solution was deposited by impregnation on the HPCM with an active substrate. As a consequence of heat treatment at 450°C, palladium nitrate decomposed to palladium oxide. Palladium oxide was applied once or several times to reach a required concentration of the metal on the carrier surface.

The activation of the highly porous cellular palladium catalyst (HPCPC) was carried out in a reactor immediately before the experiment in a molecular hydrogen flow at 50 – 55°C and initial hydrogen pressure of 0.5 MPa. The activity of the catalyst was tested on a laboratory "rocker" plant according to the method described in [5]. The material selected for the experiment was *para*-nitrotoluene (P-NT). A 1-g portion of P-NT was dissolved in 90 ml ethyl alcohol and charged into a hydration reactor. The reactor was shut with a
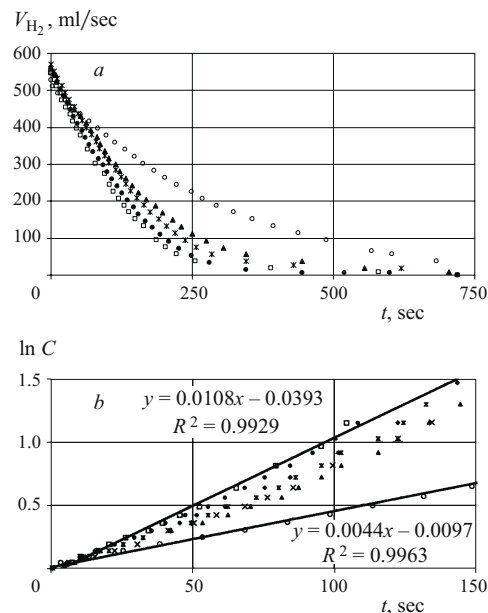
tight lid, thrice blown with hydrogen under a pressure of 0.5 MPa, then filled with hydrogen to the pressure level of 0.5 MPa and heating was switched on. After reaching a certain temperature, mixing began. The temperature in all experiments was maintained in the interval of 52 – 58°C.

In the course of the experiment, pressure gage readings (hydrogen loss with time on hydrating P-NT) were taken at a constant temperature. After the end of the experiment the reactor was opened and the reaction mixture was analyzed by high-efficiency liquid chromatography to identify its content of the resulting *para*-aminotoluene and residual nitric compound. All experiments yielded a degree of transformation over 99.99%. The experimental data are listed in Table 1 and Fig. 2.

TABLE 1

Substrate material	Catalyst weight, g	Weight content of Pd, %	Temperature, °C	W_{50}, ml/sec
SiO$_2$	26.80	2.70	56	3.04
Al$_2$O$_3$	24.29	2.44	55	2.88
TiO$_2$	26.85	2.76	55	2.62
TiO$_2$ (sulfatized)	24.60	2.35	58	2.30
ZrO$_2$	26.88	2.76	52	2.29
ZrO$_2$ (sulfatized)	22.38	1.89	53	2.53
ZnO	23.55	3.00	57	1.03

TABLE 2

Substrate material	Weight content of Pd, %	Tempe-rature, °C	Weight of Pd, g	Dura-tion, sec	Velocity constant, sec^{-1}	Load, h^{-1}
SiO$_2$	2.70	56	0.72	92	0.0151	27.19
Al$_2$O$_3$	2.44	55	0.59	99	0.0172	30.68
TiO$_2$	2.76	55	0.74	101	0.0117	24.05
TiO$_2$ (sulfatized)	2.35	58	0.58	122	0.0137	25.52
ZrO$_2$	2.76	52	0.74	121	0.0105	20.05
ZrO$_2$ (sulfatized)	1.89	53	0.42	114	0.0210	37.33
ZnO	3.00	57	0.71	202	0.0061	12.61

Time dependences of the variation in the quantity of absorbed hydrogen V_{H_2} were constructed based on the hydrogen loss (Fig. 2a) and the reaction rate was calculated for 50% transformation of initial P-NT into amine W_{50}.

The experimental data were used to calculate velocity constants for the first-order reaction using the following formula:

$$\ln \frac{C_{NC}}{C_{NC} - 0.104 \Delta p / n} = k \tau,$$

where C_{NC} is the molar content of P-NT in the solution; 0.104 is the reactor constant; $\Delta p = p_{H_2} - p_{cur}$, atm; n is the number of moles of hydrogen used for the P-NT reducing reaction; k is the first order reaction rate constant; τ is the reaction duration, sec.

Experimental data on hydrogen losses were used to calculate the concentration of P-NT based on the first-order reaction equation, dependences linearized in logarithmic coordinates were constructed, and velocity constants determined (Fig. 2b).

Analysis of the data in Table 1 and Fig. 2 shows that the highest hydration velocities (W_{50}) are achieved using the HPCPC with active substrates made of aluminum and silicon oxides and sulfatized ZrO$_2$, whereas the lowest velocity is registered for the catalysts with the ZnO substrate. Considering that the quantities of deposited palladium differed to some extent, the velocity constants and the load on the catalyst were recalculated taking into account only the active content weight (Table 2).

The maximum rate of hydration of P-NT was achieved using the HPCPC with the active substrate of sulfatized ZrO$_2$. Its velocity constant is 0.0210 sec^{-1}. The catalysts with the ZnO substrate, as could be expected, had the lowest activity. Their rate constant is 0.0061 sec^{-1}, which is nearly 3.5 times lower than in the case of sulfatized ZrO$_2$. The maximum load of nitric compounds on the catalyst was also registered in P-NT hydration on the HPCPC with the substrate made of sulfatized ZrO$_2$ (37.35 h^{-1}), which is 3 times higher than in the catalyst with the ZnO substrate. This proves the enhanced activity of the HPCPC with an acid active substrate made of sulfatized ZrO$_2$.

The experiments with the catalyst using the substrate of aluminum oxide (γ-Al$_2$O$_3$) whose acidity is lower than that of sulfatized ZrO$_2$ also demonstrated a relatively high hydration rate (rate constant 0.0172 sec^{-1}). Therefore, HPCPC with active substrates made of aluminum oxide or silicon oxide can be recommended for reducing aromatic nitric compounds, as they are less expensive than zirconium dioxide.

REFERENCES

1. É. B. Styles, *Carriers and Deposited Catalysts. Theory and Practice* [Russian translation], Khimiya, Moscow (1991).
2. Z. R. Ismagilov, R. A. Shkrabina, D. A. Arendarskii, et al., "Production and study of block catalysts with a secondary thermostable coating for cleaning waste gasses from organic compounds," *Kinet. Katal.*, **39**(5), 653 – 656 (1988).
3. D. V. Sokol'skii, "Theory of catalysis," *Zh. VKhO im. D. I. Mendeleeva*, **XII**(5), 567 – 570 (1977).
4. V. N. Efremov, A. I. Kreindel', and E. Z. Golosman, "Catalysts for production and purification of controlled atmospheres," in: *Chermetinformatsia, Ser. 13, Issue 1* [in Russian], Moscow (1975).
5. V. F. Zhilin, V. L. Zbarskii, and A. I. Kozlov, *Reduction of Aromatic Nitric Compounds. Manual* [in Russian], Izd-vo RKhTU im. D. I. Mendeleeva, Moscow (2004).